

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.				
1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE 10/29/01		3. REPORT TYPE AND DATES COVERED Final 10/1/98-9/30/01
4. TITLE AND SUBTITLE Molecular Modeling of Natural Organic Matter Interactions with Cations, Mineral Surfaces and PAHs			5. FUNDING NUMBERS N00014-99-1-0094	
6. AUTHOR(S) James D. Kubicki				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) The Pennsylvania State University Office of Sponsored Programs 110 Technology Center Building University Park, PA 16802			8. PERFORMING ORGANIZATION REPORT NUMBER FINAL 01	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) ONR Ballston Centre Tower One 800 North Quincy Street Arlington, VA 22217-5660			10. SPONSORING / MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES				
12a. DISTRIBUTION / AVAILABILITY STATEMENT APPROVED FOR PUBLIC RELEASE			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) Understanding the mechanisms of organic-mineral and organic-colloid interactions will help determine under which conditions organic contaminants will be bioavailable or sequestered. This project combines spectroscopic (<i>i.e.</i> , ATR-FTIR = Attenuated Total Reflectance Fourier-Transform Infrared) and microscopic (<i>i.e.</i> , HRTEM = High-Resolution Transmission Electron Microscopy) studies with molecular modeling, in order to help elucidate the mechanisms of organic-mineral interaction and binding. The overall goal of this research is to predict biological environmental effects from chemical knowledge of contaminated sites. Interactions of several key chemical parameters can either enhance or decrease the environmental impact of a given contaminant concentrations. Thus, this research leads to better risk assessment capability and savings in sediment management costs.				
14. SUBJECT TERMS			15. NUMBER OF PAGES 5	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT UL	

Instructions: You may use this MS Word file to submit the Technical Section of the ONR End of Year Report. Please include any images, tables, graphs, and equations into the Technical Section of the report that you feel may strengthen the technical quality of your report.. As in previous years, the Technical Section must include the *Technical Objectives*, *Technical Approach*, and *FY00 Progress*. Please complete the contract data section below so that technical information can be related to a specific contract.

Also, please save the file using the contract name as the file name (e.g. N00014-96-C-0387.doc). Instructions on sending the finished file are on the web site www.onr.navy.mil/sci_tech/engineering/33eoyreport/

When uploading the file via the web site, you will be prompted for a username and password. Please use the following:

username: onr2000
password: techreport

If you have any questions with this form or with the web site, please contact Stephanie Vogt at (703) 588-2778.

Contract Information

Contract Number	N00014-97-WX-20416
Title of Research	Molecular Modeling of Natural Organic Matter Interactions with Cations, Mineral Surfaces and PAHs
Principal Investigator	James D. Kubicki
Organization	Dept. of Geosciences - The Pennsylvania State University

Technical Section

Technical Objectives

This section will describe the objectives of the contract

Understanding the mechanisms of organic-mineral and organic-colloid interactions will help determine under which conditions organic contaminants will be bioavailable or sequestered. This project combines spectroscopic (*i.e.*, ATR-FTIR = Attenuated Total Reflectance Fourier-Transform Infrared) and microscopic (*i.e.*, HRTEM = High-Resolution Transmission Electron Microscopy) studies with molecular modeling, in order to help elucidate the mechanisms of organic-mineral interaction and binding. The overall goal of this research is to predict biological environmental effects from chemical knowledge of contaminated sites. Interactions of several key chemical parameters can either enhance or decrease the environmental impact of a given contaminant concentrations. Thus, this research leads to better risk assessment capability and savings in sediment management costs.

Specifically, this research is attempting to understand the long-range structure of the important components of natural organic matter: soot, fulvic acids, humic acids and lignin. The interactions of organic contaminants with these components controls to a large degree their fate

20011108 170

and bioavailability. In addition, fulvic and humic acids can strongly bond to aqueous cations (e.g., metals) and mineral surfaces. This bonding affects their long-range structure and their interactions with organic contaminants.

Technical Approach

This section will describe the Technical Approach taken by the contractor.

The approach taken in this project is to examine simple systems that represent important components of more complex sediment-water systems. Probable bonding mechanisms are generated from previous studies in the literature. The mechanisms deemed most important for controlling environmental fates of contaminants are then studied experimentally with analogous systems of simple compounds. The spectroscopic data of these experiments are then interpreted with molecular orbital model calculations on several possible bonding mechanisms. The results of these simplified systems are then used to help understand results on more complex experiments involving numerous natural components. Larger-scale molecular simulations of the complex systems can also be performed.

The combination of experimentation, spectroscopic analysis and molecular simulations allows one to take advantage of the strengths of each technique. For example, infrared spectra provide clues as to bonding mechanisms between natural organic matter and metals or mineral surfaces. Interpretation of these spectra is not unambiguous, however. Molecular simulations allows for more detailed and reliable interpretation of spectra. In turn, molecular simulations on their own are subject to modeling unrealistic systems. Using experimentation and spectroscopy as benchmarks for the model systems provides "ground truth" to the computational research.

Progress

This section will describe the accomplishments for Fiscal Year 2000 for the contract

Research for the Fiscal Year 2000 has focused on three main thrusts. First, field studies and experiments (Gustafsson and Gschwend, 1997) have revealed that a relatively small component of natural organic matter can control the behavior of PAHs in the environment. This component is known as "soot" or "black carbon." Field and experimental studies of soot are hampered by the fact that most soils and sediments contain only a small concentration of soot and that soot occurs as very fine-grained particles (< 1 micron). Molecular simulations have been able to take 2-D structural models of soot and produce 3-D models of long-range soot structure (Kubicki, 2000a). These models also explain the strong adsorption and sequestration of PAHs associated with soot on a molecular level (Kubicki, 2000b).

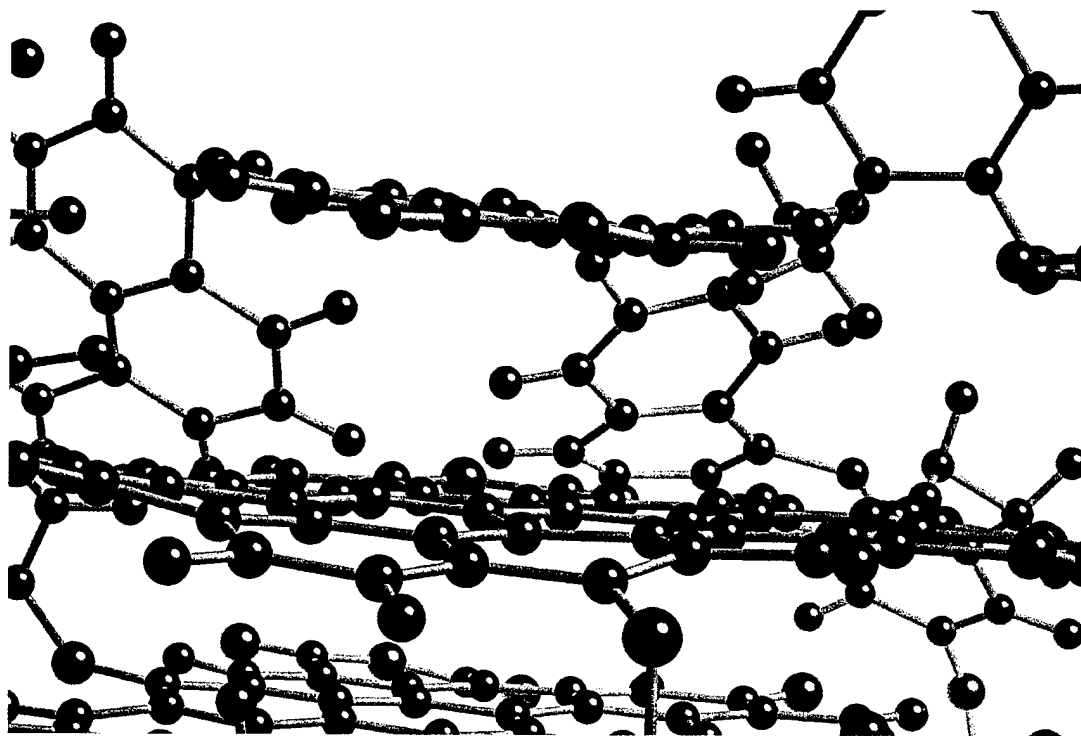


Figure 1 - Top molecule is a PAH (pyrene) that is strongly adsorbed to the surface of a soot molecule (lower layers). The pyrene-soot interaction is the same as that between layers of soot explaining the strong partitioning of PAHs from water onto soot. Simulations of PAH molecules within micropores of the soot structure demonstrate that diffusion out of a soot particle is very slow in agreement with studies that conclude sequestration and reduced bioavailability of PAHs associated with soot or similar types of natural organic matter.

The second research thrust has been to develop accurate and realistic models for mineral-water interfaces. The approach has been to use highly accurate quantum mechanical calculations on clusters and mineral surfaces to derive force field parameters that describe bonding on a hydrated surface (Kubicki et al., 2000). These force fields can then be used to model larger scale systems than can be handled with the computationally demanding quantum mechanical calculations. The structure of the mineral surface and water near mineral surfaces are critical in determining the behavior of PAHs, especially when natural organic matter contents in a sediment are low. Furthermore, an accurate picture of the mineral-water interface must be developed before effective modeling of natural organic matter binding to a mineral surface can be simulated.

Third, simulations of fulvic and humic acids in aqueous solutions have begun. The components of natural organic matter dissolve in water and can lead to enhanced solubility and transport of otherwise sparingly soluble organic contaminants. The long-range structure or conformations of fulvic and humic acids is thought to influence how much contaminant can be solubilized and the stability of the sorption. However, little is known about the conformational behavior of fulvic and humic acids in solution. Research in this group has tested the techniques necessary to realistically model dissolved organic matter as a function of solvation, pH and interaction with aqueous cations. All of these have been found to influence the long-range

structure of the model fulvic and humic acids significantly and must be accounted for during simulations of interactions with organic contaminants.

References

- Kubicki J. D. and Toplis M. J. (2001) Molecular orbital calculations on aluminosilicate tricluster molecules. *American Mineralogist*, in review.
- Kubicki J. D. and Bleam W. F. (2001) An Introduction to Molecular Modeling. In Molecular Modeling of Clays and Mineral Surfaces, J. D. Kubicki and W. F. Bleam (eds.), CMS Workshop Lectures, in press.
- Kubicki J. D. (2001) Interpretation of vibrational spectra using molecular orbital theory calculations. In Molecular Modeling Theory: Applications in the Geosciences, Reviews in Mineralogy and Geochemistry, R. T. Cygan and J. D. Kubicki (eds.) Geochemical Society of America, **42**, pp. 459-483.
- Felipe M., Xiao Y. and Kubicki J. D. (2001) Molecular orbital modeling and transition state theory in the geosciences. In Molecular Modeling Theory: Applications in the Geosciences, Reviews in Mineralogy and Geochemistry, R. T. Cygan and J. D. Kubicki (eds.) Geochemical Society of America, **42**, 485-531.
- Kubicki J. D. (2001) Integral equation formalism polarized continuum model calculations of aqueous Al^{3+} , Fe^{3+} and Si^{4+} : Correlations of calculated aqueous-phase deprotonation energies with experimental $\ln(K_a)$ and $\text{p}K_a$ values. *Journal of Physical Chemistry A*, **105**, 8756-8762.
- Hamilton, J. P., Brantley, S. L., Pantano, C. G., Criscenti, L., Kubicki, J. D. (2001) Dissolution of nepheline, jadeite and albite glasses: toward better models for aluminosilicate dissolution, submitted to *Geochimica Cosmochimica Acta*.
- Kubicki J. D. (2000) Molecular mechanics and quantum mechanical modeling of hexane soot structure and interactions with pyrene. *Geochemical Transactions*, **7**.
- Rustad J. R., Dixon D. A., Kubicki J. D., and Felmy A. R. (2000) Gas-phase acidities of tetrahedral oxyacids from *ab initio* electronic structure theory. *Journal of Physical Chemistry A*, **104**, 4051-4057.
- Kubicki J. D., Blake G. A., and Apitz S. E. (1999) Molecular models of benzene and selected PAHs in the gas, aqueous, and adsorbed states. *Environmental Toxicology and Chemistry*, **18**, 1656-1662.
- Kubicki J. D., Itoh M. J., Schroeter L. M., Nguyen B. N., and Apitz S. E. (1999) Attenuated total reflectance Fourier-transform infrared spectroscopy of carboxylic acids adsorbed onto mineral surfaces. *Geochimica et Cosmochimica Acta*, **63**, 2709-2725.
- Kubicki J. D. and Apitz S. E. (1999) Models of natural organic matter and interactions with organic contaminants. *Organic Geochemistry*, **30**, 911-927.
- Kubicki J. D., Sykes D., and Apitz S. E. (1999) *Ab initio* calculation of aqueous aluminum and aluminum-carboxylate NMR chemical shifts. *Journal of Physical Chemistry A*, **103**, 903-915.
- Schott J., Pokrovski G. S. and Kubicki J. D. (1999) Metal speciation in surficial geological fluids. In Geochemistry of the Earth's Surface, H. Armannsson (ed.), A. A. Balkema, Rotterdam, 417-419.
- Petrovski G. S., Schott J., Salvi S., Gout R., and Kubicki J. D. (1998) Structure and stability of aluminum-silica complexes in neutral to basic solutions. Experimental study and molecular orbital calculations. *Mineralogical Magazine*, **62A**, 1194-1195.
- Kubicki J. D. and Apitz S. E. (1998) Molecular cluster models of aluminum oxide and aluminum hydroxide surfaces. *American Mineralogist*, **83**, 1054-1066.

Presentations

- Kubicki J. D. and Heaney P. J. (2001) Modeling interactions of aqueous silica and sorbitol: Complexation, polymerization and association. Goldschmidt Conference, Homestead VA, May.

- Kubicki J. D. and Sykes D. (2001) Ab initio calculation of ^{17}O , ^{27}Al , and ^{29}Si NMR parameters in hydrous silica and Na-aluminosilicate glasses. Goldschmidt Conference, Homestead VA, May.
- Kubicki J. D. (2000) Molecular modeling of humic and fulvic acids, American Geophysical Union, San Francisco CA, December.
- Criscenti, L. J. and Kubicki, J. D. (2000) Molecular modeling studies of Al coordination changes during dissolution. Geological Society of America, Reno NV, November.
- Kubicki J. D. (2000) Molecular modeling of soot and interactions with polycyclic aromatic hydrocarbons. Abstracts of Papers of the American Chemical Society, Washington DC, **220**, 24-ENVR.
- Kubicki J. D. (2000) Molecular modeling of fulvic and humic acids. Papers of the American Chemical Society, Washington DC, **220**, 287-ENVR.
- Kubicki J. D. (2000) Molecular modeling of soot and interactions with polycyclic aromatic hydrocarbons. Abstracts of Papers of the American Chemical Society, San Francisco CA, **219**, 138-ENVR.
- Kubicki J. D. (1999) Molecular modeling in aqueous geochemistry. *Abstract of the American Geophysical Union*. San Francisco CA, December.
- Kubicki J. D. (1999) Molecular modeling of soot and interactions with polycyclic aromatic hydrocarbons. Ninth Annual Goldschmidt Conference, Cambridge MA, 161-162.
- Kubicki J. D. (1999) Molecular modeling of vibrational and NMR spectra of minerals and mineral surfaces. *Meeting Program and Abstracts of the 36th Annual Meeting of the Clay Minerals Society*, Purdue University, 59.
- Kubicki J. D. (1999) Coordination changes of aluminum on mineral surfaces induced by protonation/deprotonation reactions. *Abstracts of the Am. Chem. Soc.* **217**, 006-GEOC.
- Apitz S. E., Arias E., Ayers B., Clawson S. A., Lin E. W., Kirtay V. J., Kubicki J. D. and Stallard M. O. (1999) Advanced Sediment Characterization: Case Studies, *Characterization and Treatment of Sediments 4: International Congress*, Antwerp, Belgium, September 15-17.
- Kubicki J. D. and Apitz S. E. (1998) Models of PAH interactions with different carbonaceous and organic substrates. *Abstracts of the Am. Chem. Soc.* **215**, GEOC-073.